

February 18, 1981

Mr. Robert J. Courchaine
Chief, Water Division
Department of Natural Resources
Stevens T. Mason Building
Box 30028
Lansing, MI 48909

US EPA RECORDS CENTER REGION 5



402887

Dear Mr. Courchaine:

As part of the requirements of Section C, Process Waste Characterization Study, of Pennwalt's Final Order of Abatement, a detailed procedure used for the characterization of Process 45 - Triethylamine oxide/Diethylhydroxylamine, is attached.

A liquid chromatographic method for the analysis of hexadecyl mercaptan and the corresponding disulfide is nearly complete, with the exception of a few minor details.

Since this product is made very infrequently, we are confident that we will have a fully completed method available by the end of the second quarter for the next projected production run.

Attempts at development of a method for Methane Sulfonyl Chloride and Methane Sulfonic Acid have not been nearly as successful. To date, we have been unable to obtain consistent results using the same technology that has been so successful for amines and their derivatives.

These two compounds are so highly polar and acidic that the gas chromatography-purge and trap system utilized for much of the work during the study has so far been unsuccessful.

Liquid chromatography is also complicated by the fact that neither the Methane Sulfonic Acid or the Methane Sulfonyl Chloride is ultra violet active; the use of refractive index detection is both insensitive at the desired levels and unreliable.

RECEIVED

FEB 20 1981

PTE. MOUILLEE S.G.A.

Mr. Robert J. Courcaine
Chief, Water Division
Department of Natural Resources

ATTACHMENT NO. 1

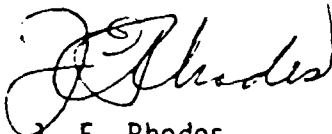
-2-

2 OF 15

We are currently experimenting with the liquid chromatography of aromatic amine derivatives of Methane Sulfonic Acid and Methane Sulfonyl Chloride, using ion exchange separation techniques, combined with an ultraviolet detector. The results, so far, have been encouraging. We will keep you advised of our progress.

Sincerely,

PENNWALT CORPORATION



J. E. Rhodes
Manager, Technical Department

cc: Paul Zugger
David Batchelor
Roy Schrameck

GC PROCEDURE FOR DIETHYLHYDROXYLAMINE IN WATERSCOPE:

To analyze waste water for DEHA and/or its decomposition products to the 1ppm level.

APPARATUS:

A CDS (Chemical Data Systems) model 310 trapping concentrator (fitted with their desorber and standard traps) with necessary hardware to mate to the GC used.

GC

Perkin Elmer Sigma I system fitted for on column injection using a 1/4" glass column with split disector flow to FID and NPD. Carrier gas used - Helium at 75 psig.

GC COLUMN

Glass 6 feet x 2mm ID
Chromosorb 102 with 7% Triton x 305 and 0.5% KOH (80-100 Mesh)

Syringe: Hamilton CR 700-200

PROCEDURE:

The CDS 310 is mated to the Sigma I by a 2" x 1/8" to 1/16" ss connector. It replaces the GC septum retaining nut, and is connected to the CDS 310 valve assembly discharge with a 1/8" Swagelok tube fitting. Follow the CDS manual for set up of necessary piping of carrier gas and air supply. The CDS system will control the carrier gas.

Set up the GC with the 6 ft. glass column specified above so the column will extend all the way through the GC injection port and seat against a septum inside the CDS connecting adaptor. The CDS parameters are as follows:

Carrier gas 30ml/min. at 75 psig

Desorber flow 40ml/min.

Desorber Temperature - 200°C - Heat 5 minutes - Cool 8 minutes

*Valve Temperature 200°C (approximately)

*CAUTION (refer to the manual on valve operating procedures)

Trap temperature - 200°C - 8 minutes

4 O.E. 15

PROCEDURE (continued)

The Sigma I system procedure is Method #2 (see Attachment #1) and is used with a dual detection arrangement using a detector splitter 50/50 to the FID and NPD.

The column and trap system must be conditioned with repeated injections of the cleanest water obtainable. Use 2ul of water direct through the CDS "column injection port" until a reproducible scan is obtained. (See Attachment #2).

To condition the traps and desorber chamber, inject 10ul of water directly into the desorber chamber and heat for 5 minutes onto trap and cool 8 minutes. (The more water injected the longer the heat and cool cycle will have to be). The trap is then heated for about 6 to 8 minutes at 200°C backflushing onto the column.

Repeat runs until a consistent scan similar to Attachment #3 is obtained. A new column may take two or three days to condition.

Once a good blank run has been obtained, a sample run is first made using 2ul of sample injected directly to the column. Attachment #4 shows a typical scan of a test solution of 52ppm of a fresh DEHA mix through the CDS trap system. As the sample ages it will change to a combination of the peaks at 6.48, 7.90 and 8.37. If the DEHA is about 20-25ppm or less, it will decompose almost completely with the peak at 6.48 being the only one of measurable amounts. If nothing is detected, or very low response using 2ul, then inject up to 10 to 20ul into the desorber and trap system to concentrate and backflush to column.

The method must be calibrated with fresh standards.

BEF:blw
2/17/81

TO THE 1 PPM LEVEL IN WASTE WATER.

Attachment #1

COL-- GLASS 6FT 2MM ID CHROMOSORB 102 (80-100 mesh)

7% TRITON 305 + 0.5% KOH

L2

LST2

ATTACHMENT NO 7

5 OF 15

METHOD 2

ANALYZER CONTROL

INJ TEMP 200
DET ZONE 1,2 250 25
AUX TEMP 25
FLOW A.B 30 5
INIT OVEN TEMP, TIME 75 0

TEMP RATE TIME
225 12.0 8

DATA PROC

STD WT, SMP WT 1.0000 1.0000 1
FACTOR, SCALE 1 0
TIMES 20.40 0.00 11.10 14.50 327.67 327.67
SENS-DET RANGE 200 20 0.00 2 0 0
UNK, AIR 1.000 0.00
TOL 0.0000 0.050 1.0
REF PK 0.000 0.00 0.00 0.00
STD NAME

EVENT CONTROL

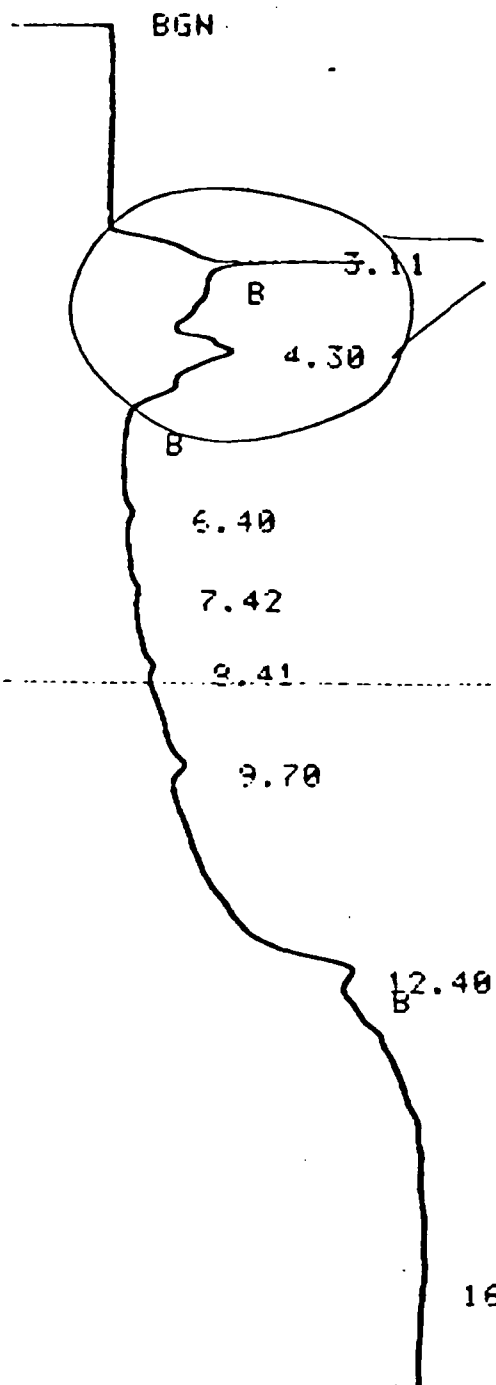
ATTN-CHART-DELAY 3 10 0.01

PUN 7 2MM ID GLASS 6FT C102-242-7-0,5KOH

SENSITIVITIES 200 20

2ul Blank - Direct injection
NPD - Bead 410 Range 1 Att. 1
Hydrogen 9 psig
FID - Air 30 psig
Hydrogen 26 psig

This is associated with water



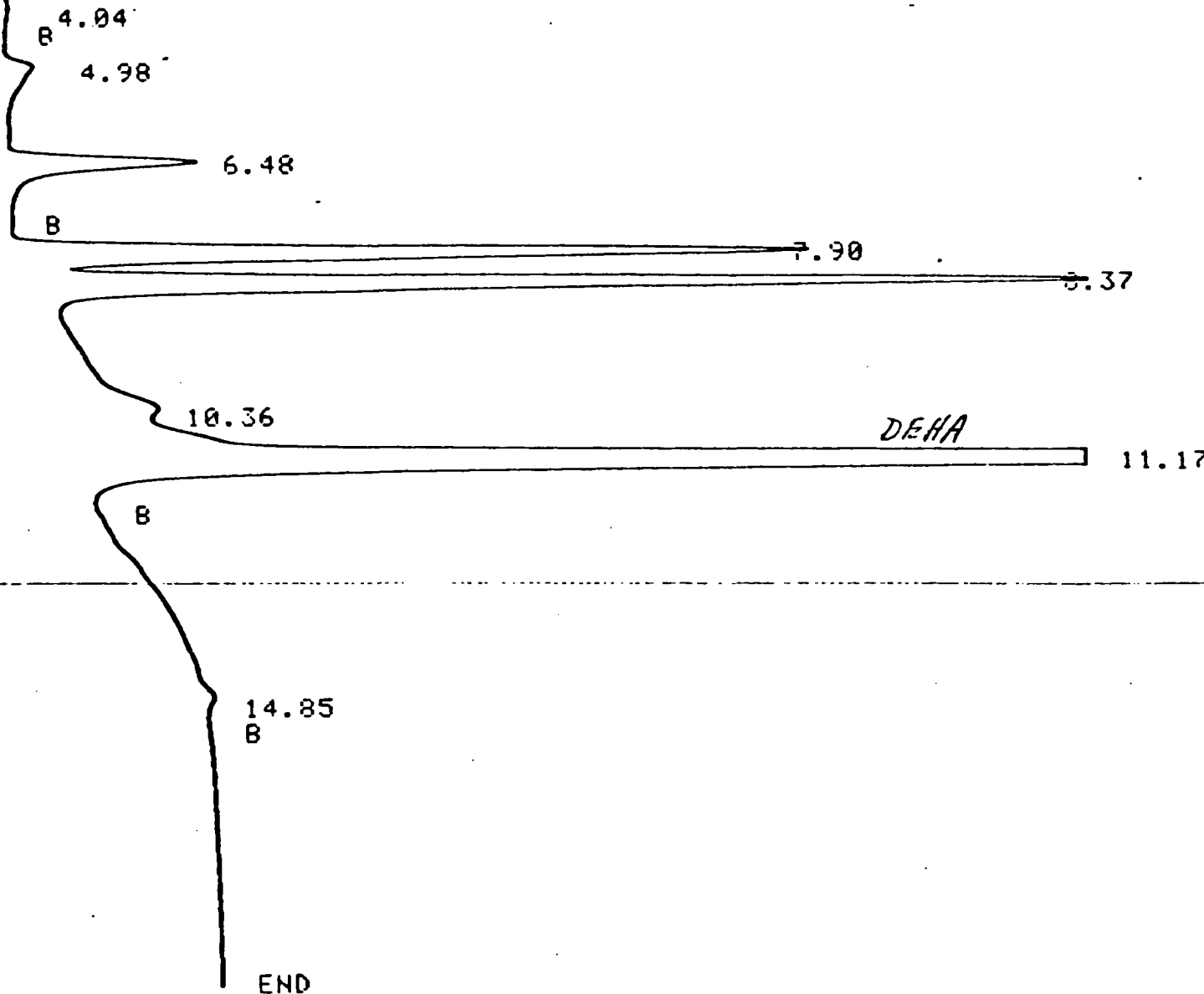
Attachment # 3

Desorber:
Heat 7mins @ 2
Cool 28mins
TRAP: Heat 6mins @

ATTACHMENT NO 7
7.0E15



ATTACHMENT N. 7
8 OF 15



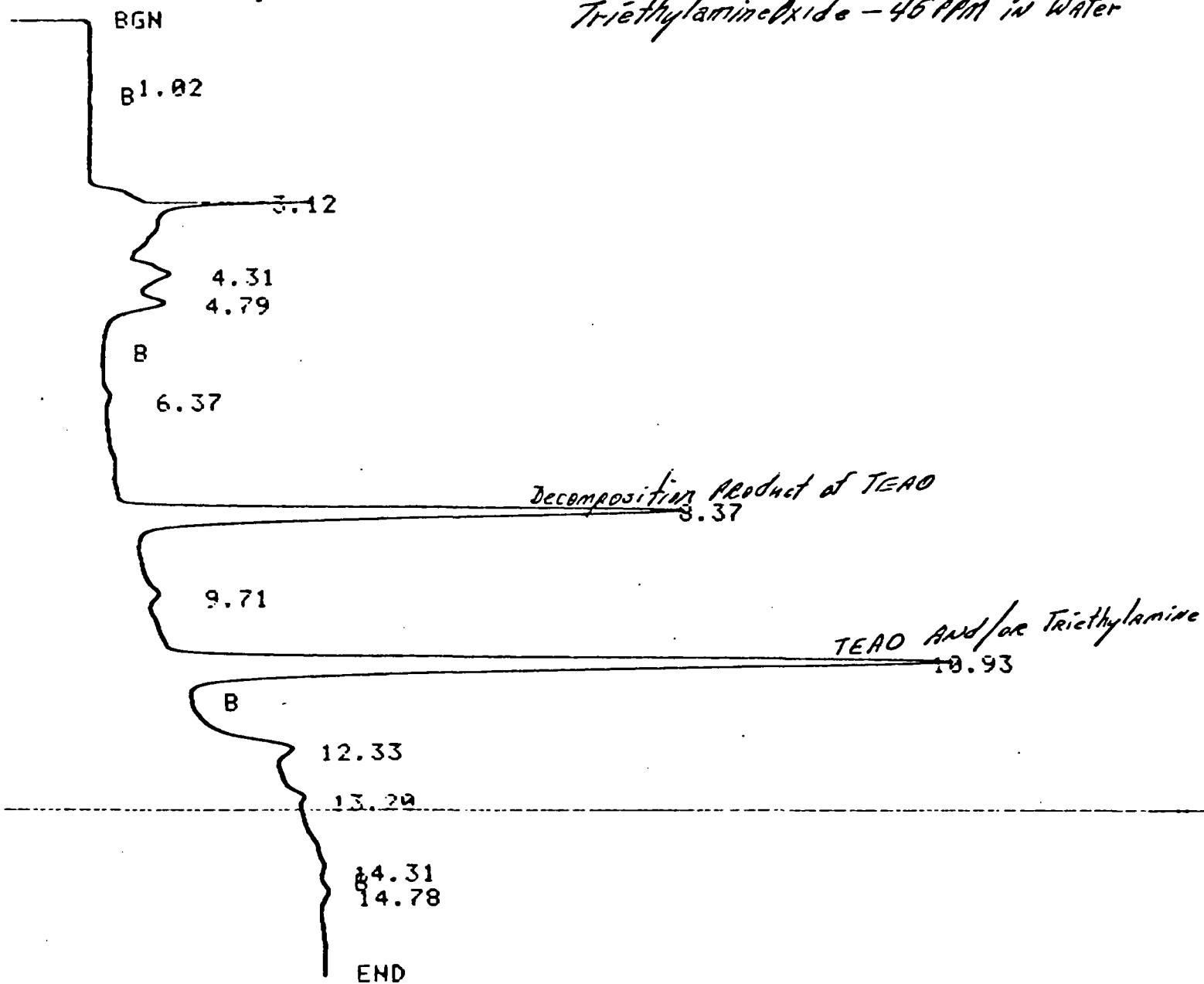
ANAL 1 DET 1 METH 2 2 FILE 47

9 05 '5

PUN 2 GLASS 6FT 2MMID DEHA COLUMN

SENSITIVITIES 200 20

2 µl (Direct injection)
Triethylamine oxide - 46 ppm in water



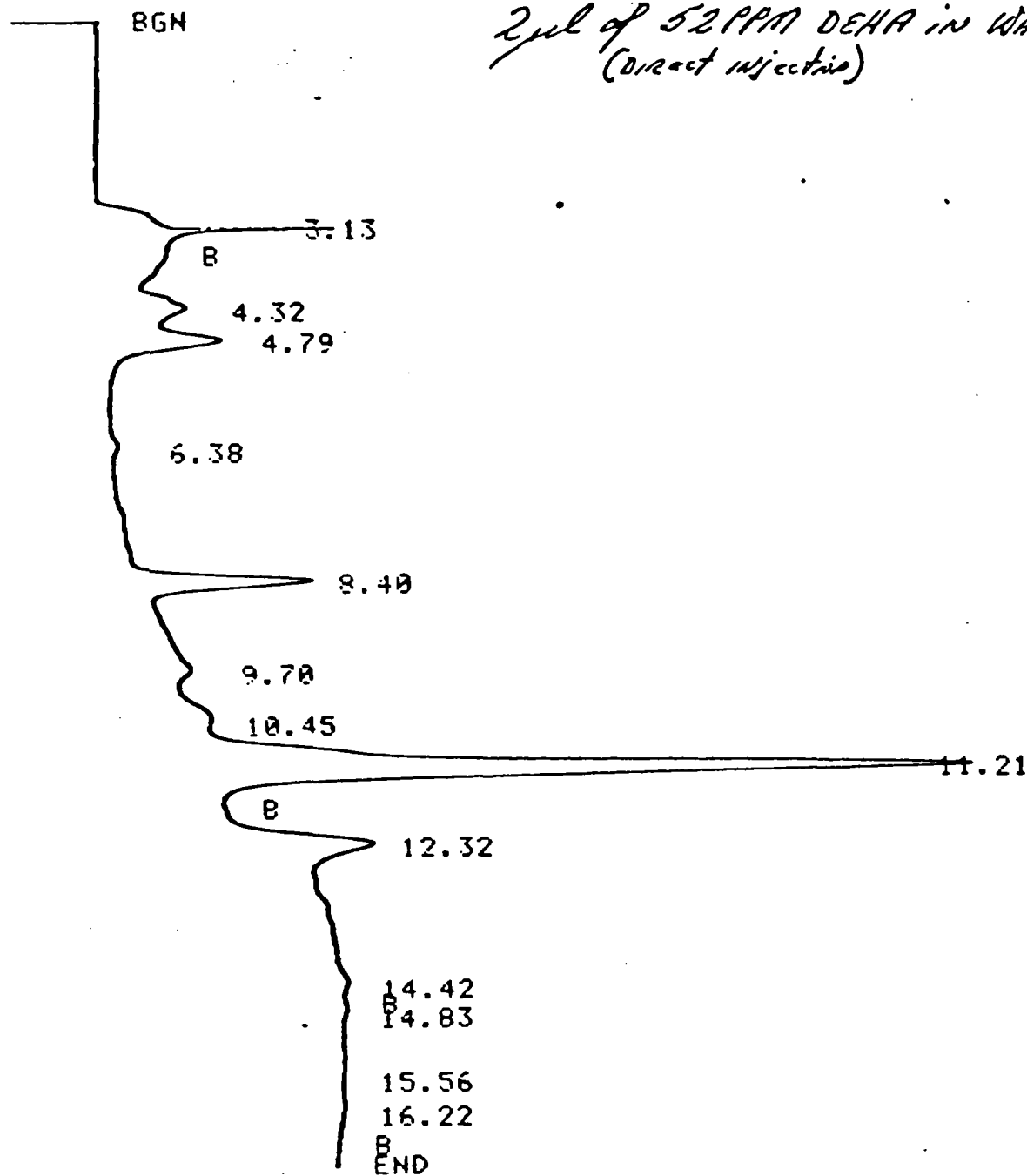
RUN 5 GLASS 6FT 2M... DEHA COLUMN

ATTACHMENT NO7

SENSITIVITIES 200 20 NPD Range 1 ATTEN 3

10 OF 15

*2 µl of 52 PPM DEHA in Water (3 weeks old)
(Direct injection)*



PUN 7 GLASS 6FT 1 ID DEHA COLUMN

Attachment #7

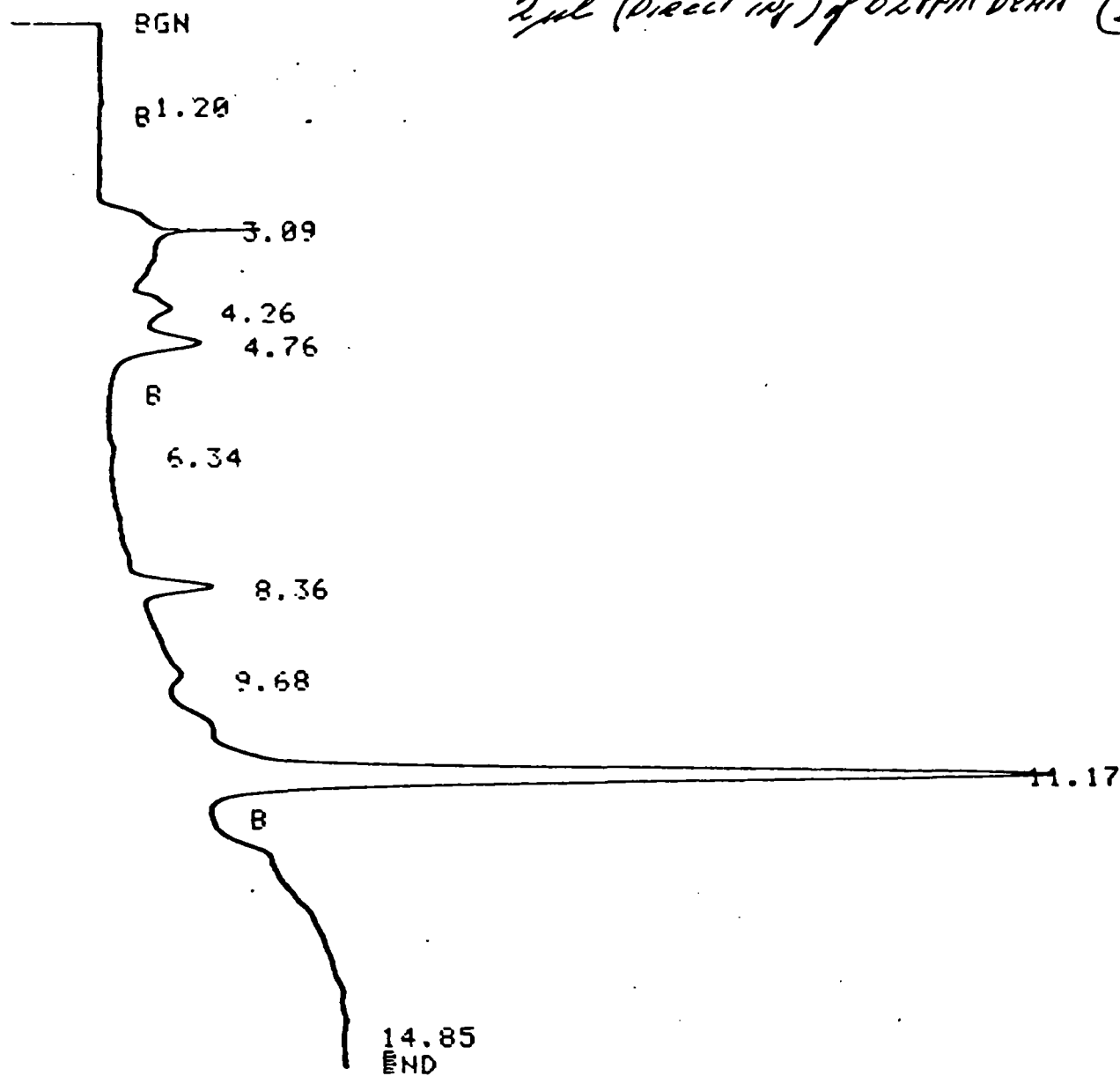
ATTACHMENT NO 7

SENSITIVITIES 200 20

NPD Range 1 Atten 3

11 DE 15

2ul (Direct inj) of 521PM DEHA (1 Day old)



RUN 9 GLASS 6FT 2 ID DEHA COLUMN

H-TACHMENI " 0

ATTACHMENT NO 7

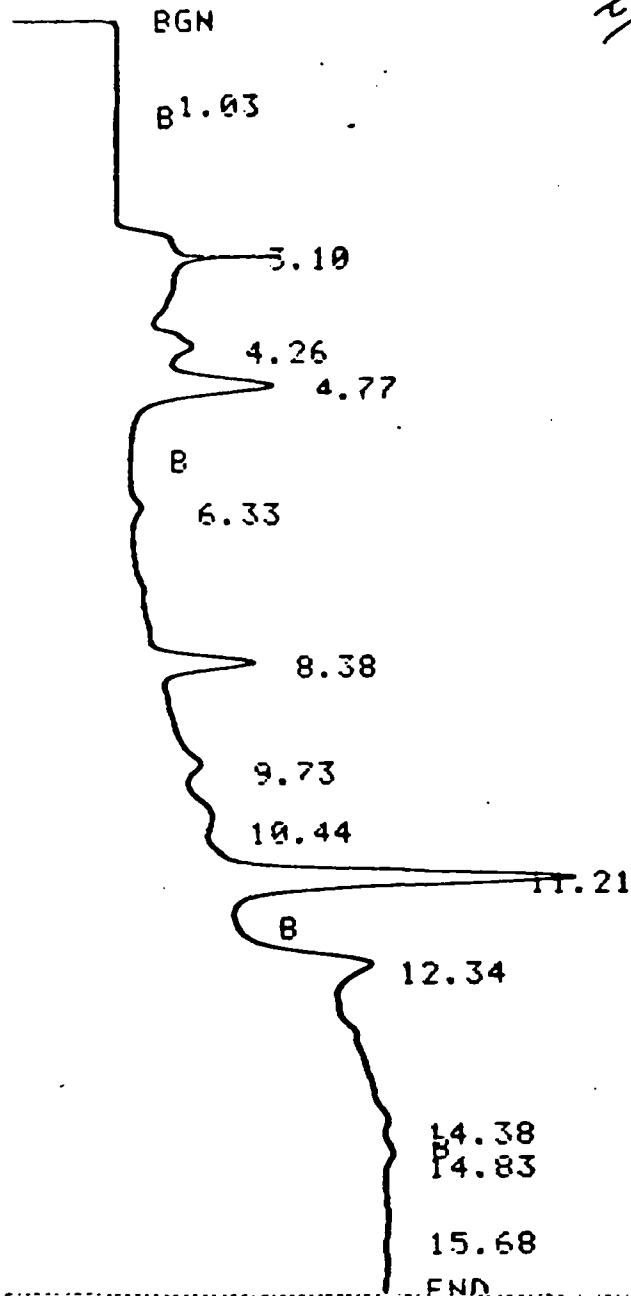
SENSITIVITIES 200 20

NPD Range 1 Atten 3

12 DE 15

2 µl (Direct injection) 18 PPM DEHA

(Fresh Mix) < 1 hr old



PUN 10 GLASS 6FT 2 10 DEHA COLUMN

A. Attachment #9

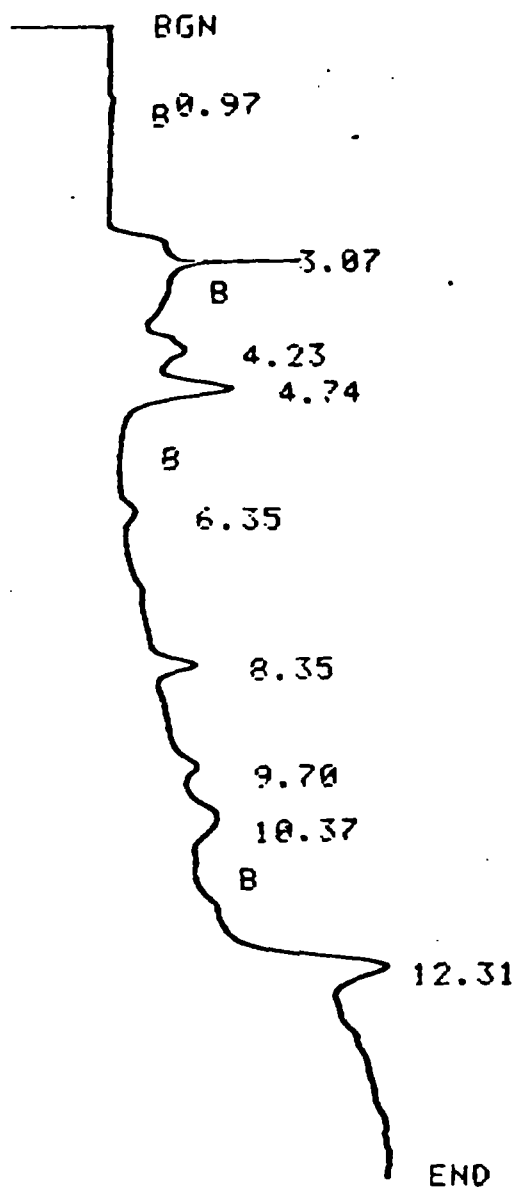
ATTACHMENT NO.7

SENSITIVITIES 200 20

NPD Range 2 Atten 3

13 J.F. 15

2ul (Direct injection) 18PPM DEHA
(18 days old)



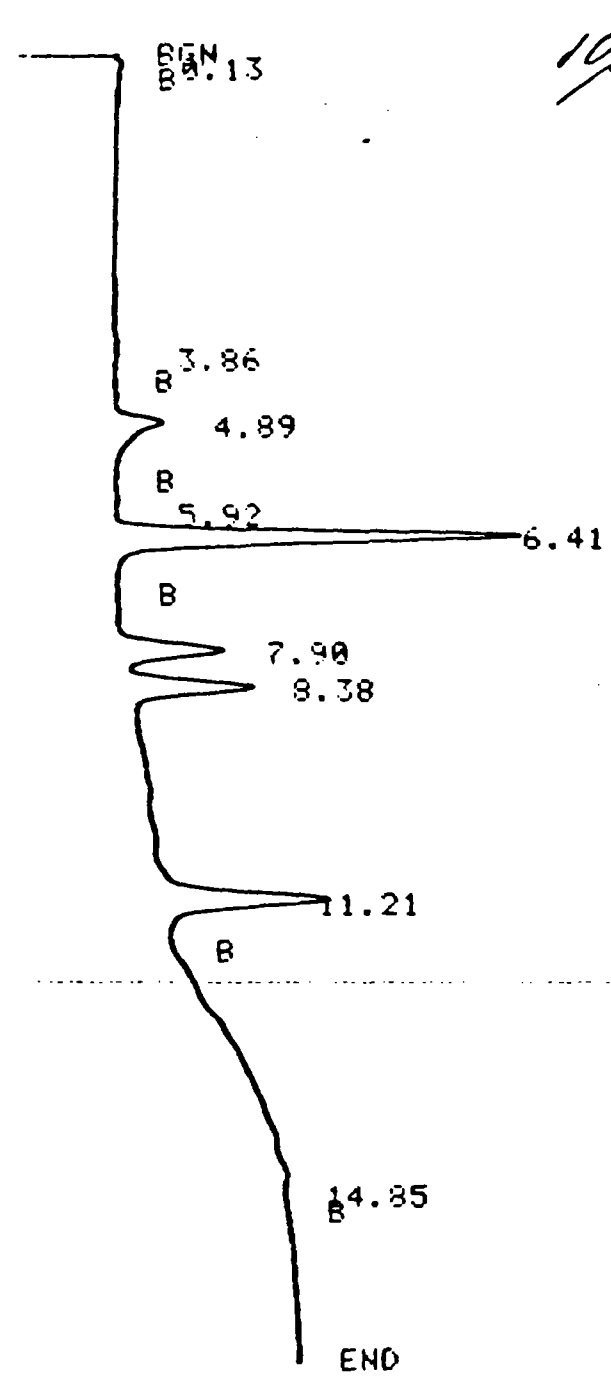
RUN 13 GLASS 6FT 2M...0 DEHA COLUMN

Att. ment #10

SENSITIVITIES 200 20

APD Range #1 Atten 3

ATTACHMENT NO. 2
14 DE 15



10ul (injected in desorber/tray)
18PPM DEHA in water
(sample 1 Day old)

ANAL 1 DET 1 MET 2 2 FILE 51

ATTACHMENT NO. 1

PUN 12 GLASS 6FT 2MMID DEHA COLUMN

15 SEP 1955
Attachment #11

SENSITIVITIES 200 20

NPD Range I Attenu 3

10µl (injected in Densher/Tray)
18PPM DEHA (18 Days old)

BEN
B 0.14

4.00

B
4.95

6.45

7.93

8.40

9.87

END

WASTE WATER
NPDES MONITORING

AMPLING POINT: 001 WYE ST. DATE ANALYZED: DATE REPORTED:

TIME OF SAMPLING: GRAB DATE:

TEMPERATURE: °C °F

TESTED BY:				APPROVED BY:			
ABOVE LIMITS	1.	2.	3.	4.	5.	6.	

SM - STANDARD METHODS OF WATER AND WASTE WATER, 14th EDITION
STORET - EPA METHODS

NOTE: $10^6 = 1,000,000$

PARAMETER	ANSWER	LIMIT	PARAMETER	ANSWER	LIMIT
1. mg/l suspended solids =			4. mg/l ammonia as N =		
2. mg/l residual chlorine =			5. pH =		
3. mg/l chloride =			6. mg/l C.O.D. =		

1. S.S. - Wed.
SUSPENDED SOLIDS - GRAB - mg/l METHOD SM - 208D

Gross wt. =									Results
(-)									
Tare wt. =			X	10^6	÷	ml sample	=		mg/l S.S.
Ppt. wt. =			X	10^6	÷	100	=		

2. Res. Cl₂ - Wed.
RESIDUAL CHLORINE - GRAB - mg/l METHOD SM - 409E
a. 1 ml of FeSO₄·(NH₄)₂SO₄ = 100 micrograms of residual chlorine

Results									
b. mg/l Res. Cl ₂	=	Titer	X	Micrograms/ml	÷	ml sample			
	=		X	100	÷	100			

3. Cl - Wed.
CHLORIDES - GRAB - mg/l METHOD SM 408A

	Results										
	mg/l Cl	=	ml AgNO ₃	X	N AgNO ₃	X	mcw	X	10 ⁶	÷	ml sample
		=		X	0.085528		0.035453	X	10 ⁶	÷	100

4. NH₃-N - Wed.
AMMONIA AS NITROGEN - GRAB - mg/l METHOD STORET 00610

a. Absorbance Method:
Spectrophotometric absorbance reading = = mg N

Results									
mg/l NH ₃ -N	=	mg N	X	1,000	÷	$\frac{10}{400 \times 500}$			or 8 ml net sample
	=		X		÷	8			

b. Titration Method:

Results	=	ml H ₂ SO ₄	X	N H ₂ SO ₄	X	mew	X	10 ⁶	÷	$\frac{480}{400 \times 500}$
mg/l NH ₃ -N	=		X	0.02	X	0.01401	X	10 ⁶	÷	384

5. pH - Wed.
pH - GRAB METHOD STORET 00400 pH =

6. C.O.D. See Page 2

Page 2 - 001 MONITORING

GRAB DATE: _____
ANALYSIS DATE: _____

6. C.O.D. - Tues., Thur., Fri.

CHEMICAL OXYGEN DEMAND - GRAB - mg/l METHOD STORET 0340

a. Standardization: Normality of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$

N $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$	=	ml $\text{K}_2\text{Cr}_2\text{O}_7$	X	N $\text{K}_2\text{Cr}_2\text{O}_7$	\div	ml $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$
--	---	--------------------------------------	---	-------------------------------------	--------	---

	=		X		\div	
--	---	--	---	--	--------	--

b. C.O.D. - mg/l

Results mg/l C.O.D.	=	(Blank-Sample)	X	N $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$	X	mew	X	10^6	\div	ml sample
	=	(-)	X		X	0.008	X	10^6	\div	50
	=		X		X	0.008	X	10^6	\div	50

6.	C.O.D. See Page 2
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COMPOSITE DATE: _____
ANALYSIS DATE: _____

6. C.O.D. - Tues., Thur., Fri.

CHEMICAL OXYGEN DEMAND - COMPOSITE - mg/l METHOD STORET 0340

a. Standardization: Normality of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$

N $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$	=	ml $\text{K}_2\text{Cr}_2\text{O}_7$	X	N $\text{K}_2\text{Cr}_2\text{O}_7$	\div	ml $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$
	=	25	X		\div	

b. C.O.D. - mg/l

Results mg/l C.O.D.	=	(Blank-Sample)	X	N $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$	X	mew	X	10^6	\div	ml sample
	=	(-)	X		X	0.008	X	10^6	\div	50
	=		X		X	0.008	X	10^6	\div	50

5.	pH - Daily			
	pH - COMPOSITE - METHOD STORET 00400	pH	=	

WASTE WATER
NPDES MONITORING

SAMPLING POINT: 005 POND

DATE ANALYZED: _____

DATE REPORTED: _____

TIME OF SAMPLING: _____

COMPOSITE DATE: _____

GRAB DATE: _____

TEMPERATURE: _____ °C _____ °F

TESTED BY: _____

APPROVED BY: _____

SM - STANDARD METHODS OF WATER AND WASTE WATER,
14th EDITION
STORET - EPA METHODS

	1.	2.	3.	4.	5.	6.
ABOVE LIMITS						

NOTE: $10^6 = 1,000,000$

PARAMETER	ANSWER	LIMIT		ANSWER	LIMIT
1. mg/l suspended solids =		35	4. mg/l ammonia as N =		1.0
2. mg/l residual chlorine =		1.0	5. pH =		6.5-9
3. mg/l chloride =			6. mg/l C.O.D. =		

1. S.S. - Mon., Tues., Wed., Thur., Fri.

SUSPENDED SOLIDS - GRAB - mg/l METHOD SM - 208D

Gross wt. =										
(-)										
Tare wt. =			X	10^6	\div	ml sample	=	Results		
Ppt. wt. =			X	10^6	\div	100	=	mg/l S.S.		

2. Res. Cl_2 - Daily - 7 days/wk.

RESIDUAL CHLORINE - GRAB - mg/l METHOD SM - 409E

a. 1 ml of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 = 100$ micrograms of residual chlorine.

Results										
b. mg/l Res. Cl_2	=	Titer	X	Micrograms/ml	\div	ml sample				
	=		X	100	\div	100				

3. Cl - Mon., Wed., Fri.

CHLORIDES - COMPOSITE - mg/l METHOD SM - 408A

Results										
mg/l Cl	=	ml AgNO_3	X	N AgNO_3	X	mew	X	10^6	\div	ml sample
	=		X	0.085528	X	0.035453	X	10^6	\div	5

4. $\text{NH}_3\text{-N}$ - Mon., Wed., Fri.

AMMONIA AS NITROGEN - COMPOSITE - mg/l METHOD STORET 00610

a. Absorbance Method:

Spectrophotometric absorbance reading = = mg N

Results										
mg/l $\text{NH}_3\text{-N}$	=	mg N	X	1,000	\div	$400 \times \frac{10}{500}$				or 8 ml net sample
	=		X	1,000	\div	8				

b. Titration Method:

Results										
mg/l $\text{NH}_3\text{-N}$	=	ml H_2SO_4	X	N H_2SO_4	X	mew	X	10^6	\div	$400 \times \frac{480}{500}$
	=		X	0.02	X	0.01401	X	10^6	\div	384

5. pH - Daily - 7 Days.

pH - COMPOSITE METHOD STORET 00400

pH =

6. C.O.D. See Page 2

6. C.O.D. - Tues., Thur., Fri.
CHEMICAL OXYGEN DEMAND - COMPOSITE - mg/l METHOD STORET 0340

a. mg/l Cl from step 3, page 1 = _____ mg/l

b. Calculation of how much HgSO_4 to add to sample:

1. A 50 ml sample is used for C.O.D.

2. $\text{mg/l Cl} \div 20 = \div 20 =$ _____ mg Cl in 50 ml sample.

3. $\text{mg Cl in 50 ml} \div 1000 =$ _____ grams Cl in 50 ml sample

4. $\text{g Cl in 50 ml} \times 10 =$ _____ g HgSO_4 to add to C.O.D. sample

Enough HgSO_4 is added to take care of 10 x Cl present.

c. Calculation of how much NaCl to add to Salt Correction Sample:

1. $\text{g Cl in 50 ml} \times 1.6485 =$ _____ g NaCl to add to Salt Correction Sample

2. $1.6485 =$ NaCl/Cl mol. wt. ratio

d. Standardization: Normality of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$

N $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$	=	ml $\text{K}_2\text{Cr}_2\text{O}_7$	X	N $\text{K}_2\text{Cr}_2\text{O}_7$	\div	ml $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$
	=	25	X		\div	

e. C.O.D. on sample before salt correction:

mg/l C.O.D.	=	(Blank - Sample)	X	N $\text{K}_2\text{Cr}_2\text{O}_7$	X	mew	X	10^6	\div	ml sample
	=	(-)	X		X	0.008	X	10^6	\div	50
	=		X		X	0.008	X	10^6	\div	50

f. C.O.D. on salt correction sample:

mg/l C.O.D.	=	(Blank - Sample)	X	N $\text{K}_2\text{Cr}_2\text{O}_7$	X	mew	X	10^6	\div	ml sample
	=	(-)	X		X	0.008	X	10^6	\div	50
	=		X		X	0.008	X	10^6	\div	50

g. Net mg/l C.O.D. in 005:

Results mg/l C.O.D.	=	mg/l C.O.D. on uncorrected sample (Step e)	-	mg/l C.O.D. on salt corrected sample (Step f)
	=		-	

LABORATORY REPORT - OUTFALL 006NPDES MONITORING

Date Sampled: Comp: _____ Analyzed and Reported: _____

" " Grab: _____ Signed: _____

<u>PARAMETER</u>	<u>UNITS</u>	<u>METHOD</u>	<u>SAMPLE</u>	<u>OUTFALL 006</u>			<u>SOUTH INTAKE</u>	<u>NON- CONTACT</u>
				<u>AVE.</u>	<u>MAX.</u>	<u>RESULT</u>		
Temp.	°F		-			_____		
Res. Cl ₂	mg/l	SM-409E	Grab		0.5	_____		
Chlorides	mg/l	SM-408A	Comp		147*	_____		
NH ₃ -N	mg/l	EPA-00610	Grab	1.5	3.0	_____		_____
Sus. Solid	mg/l	SM-208D	Comp.	6.3	9.5*	_____		
COD	mg/l	SM-508	Comp.			_____		
BOD ₅	mg/l	SM-507	Comp.	6.3	9.5	_____	_____	
BOD ₅ DATE SAMPLED		-	-			_____	_____	
Phenol	ug/l	SM-510C	Comp.		200	_____		
Sulfides	mg/l	SM ₁ -228A	Comp.			_____		

pH CHECK

LAB _____

RECORDER _____

METER _____

GATEHOUSE _____

SM = Standard Methods, Water and Waste Water 14th Edition

SM₁ = Standard Methods, Water and Waste Water 13th Edition

EPA = Environmental Protection Agency Manual 1974 Edition

*NPDES limits are expressed in Net #/Day. Limits shown are based on an average flow of 7.2 MGD. Reported values are on a gross basis.

DISTRIBUTION: B100, E40, G96, G100, K4, L5, M41, M47, P28, R8, S72, Shift Supt. W